New NIR methine dyes as sensing agents for ammonia

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Abstract

New NIR methine dyes with modified polyene chain belonging to cyanine and triphenylmethane groups has been synthesised and tested for the sensitivity to ammonia. It was found that the dyes are reversibly sensitive to ammonia and also to some amines in ethanol and ethanol–water solutions. The dyes may be also used as pH indicators in the basic pH region. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: NIR methine; Acid–base indicators; Modified polyene chain

1. Introduction

Photometric devices using a chemical transducer in the form of solid matrix-supported dyes represent a promising class of instruments for gas monitoring over a wide range of concentrations. Dyes absorbing in the region 700–900 nm are of particular importance since the absorbance of most tested materials is minimal in this region and does not interfere with the absorbance of a NIR chromophore. Furthermore, the absorption wavelength of the dyes matches to the emission wavelength of laser diodes and the optical transmission window of communication fibres.

Recently, attempts have been made to develop sensors in the visible region for ammonia in both gas and liquid phases [1–6]. A synthesis of acid–base indicators absorbing in the NIR region has been published recently [7–9].

Our long-term aim is to find dyes suitable for use as transducers in distributed fibre optic ammonia sensors. Metal complexes, squaraine dyes and methine dyes have been synthesised and tested [10,11]. This paper describes the synthesis of new methine NIR dyes belonging to cyanine and triphenylmethane groups and testing their sensitivity to ammonia and to some amines

in ethanol and ethanol–water solutions. Usability of the dyes as pH indicators has been tested as well.

2. Experimental

2.1. Preparation of the dyes

2.1.1. Cyanine dyes

Dyes of the cyanine group D1a-c were prepared by condensing a 4-(dimethylaminomethylene)-5-oxo-2-furfurylidenedimethyliminium perchlorate with an appropriate salt, e.g. 3-ethyl-2-methyl-benzothiazolium iodide, 1,2,3,3 - tetramethyl(3H)indolium iodide and 2 - methyl-4,6-diphenylpyrylium perchlorate. The general reaction scheme is represented in Fig. 1. The procedure for the synthesis was the following: A mixture of 1.0 g (0.34 mmol) of 4-(dimethylaminomethylene)-5-oxo-2-furfurylidene-dimethyliminium perchlorate, 0.68 mmol of appropriate salt and 0.66 g (0.68 mmol) of anhydrous potassium acetate in 20 ml of acetic anhydride was heated under reflux for 1 h. After cooling down to room temperature, precipitation of the products was completed by addition of diethylether. The crude product was washed with acetic acid, diethylether and repeatedly recrystallised from ethanol:diethylether (10:5) mixture. The basic characteristics of the dyes are summarised in Table 1.

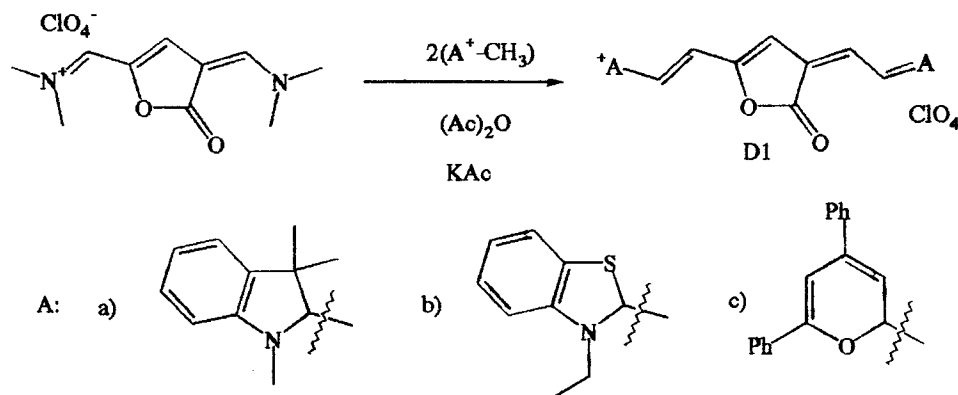* Corresponding author. Tel.: + 421 7 5325530; fax: + 421 7 393198; e-mail: simon@cvtstu.cvt.stuba.sk

Fig. 1. Reaction scheme for the synthesis of the cyanine dyes D1a-c.

Table 1
Basic characteristics of the dyes (molar weight, melting point, yield and maximum wavelengths in ethanolic solution)

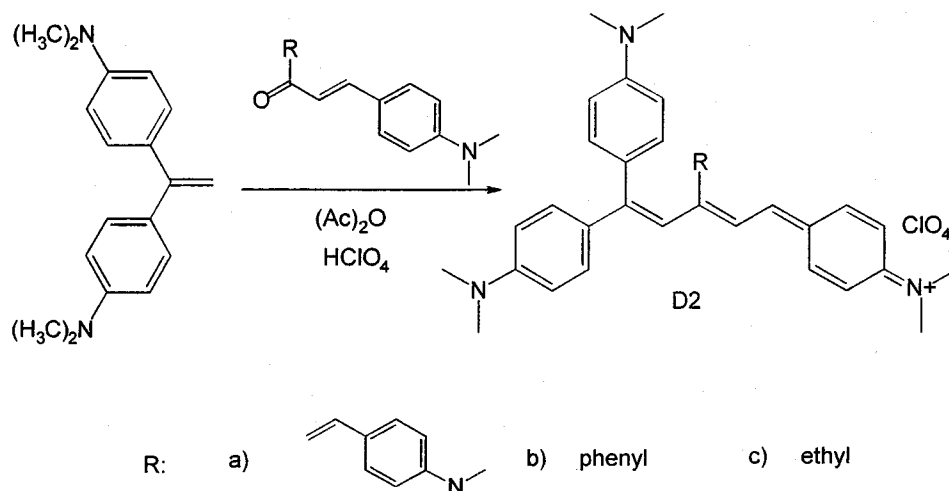| Dye	Formula	M.W. (g mol^{-1})	M.p. (°C)	Yield (%)	λ_{max} (nm)
D1a	$C_{30}H_{31}ClN_2O_6$	551.04	263	62	726
D1b	$C_{26}H_{23}ClN_2S_2O_6$	559.05	269	55	714
D1c	$C_{42}H_{29}ClO_8$	697.14	260	39	684
D2a	$C_{39}H_{45}ClN_4O_4$	668.91	170	53	696, 807
D2b	$C_{35}H_{38}ClN_3O_4$	600.16	185	60	697, 808
D2c	$C_{31}H_{38}ClN_3O_4$	552.11	205	45	694, 809

Fig. 2. Reaction scheme for the synthesis of the triphenylmethane dyes D2a-c.

2.1.2. Ttriphenylmethane dyes

These dyes labelled as D2a-c were prepared by condensing 1,1-bis(4-dimethylamino-phenyl)ethylene with an appropriate ketone, e.g. (4-dimethylaminophenyl) penten-3-on, 4-dimethylaminochalcone and bis(4-dimethylaminobenzal)acetone. The general reaction scheme is represented in Fig. 2. The procedure for the synthesis was as follows: A mixture of 1.0 g (3.75 mmol) of 1,1-bis(4-dimethylaminophenyl)ethylene and 3.75 mmol of appropriate ketone in 10 ml of acetic anhydride was treated with a solution of 0.26 g (0.19 mmol) of 71% perchloric acid in 10 ml of acetic anhydride. The blue mixture was refluxed for 70 min with occasional swirling. After cooling down to room temperature, the precipitation of the products was completed by addition of diethylether. The crude product was collected, washed with acetic acid followed by ether and repeatedly recrystallised from acetone/diethylether (10/5 v/v) mixture.

The preparation of 4-(dimethylaminomethylene)-5-oxo-2-furfurylidenedimethyl iminium perchlorate has been published in [12]. The synthesis of 2-methyl-4, 6-diphenylpyrylium perchlorate is described in [13]. The ketones ((4-dimethylaminophenyl)penten-3-on, 4-dimethylaminochalcone, bis(4 - dimethylamino - benzal) acetone) were prepared by the literature procedures
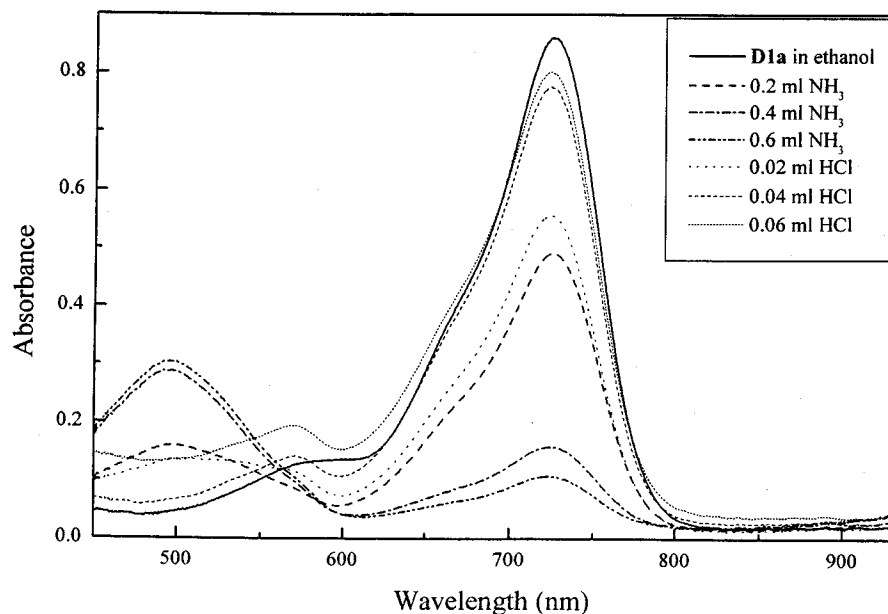
Fig. 3. Solution spectra of the dye D1a in the presence of ammonia and its reversibility by HCl.
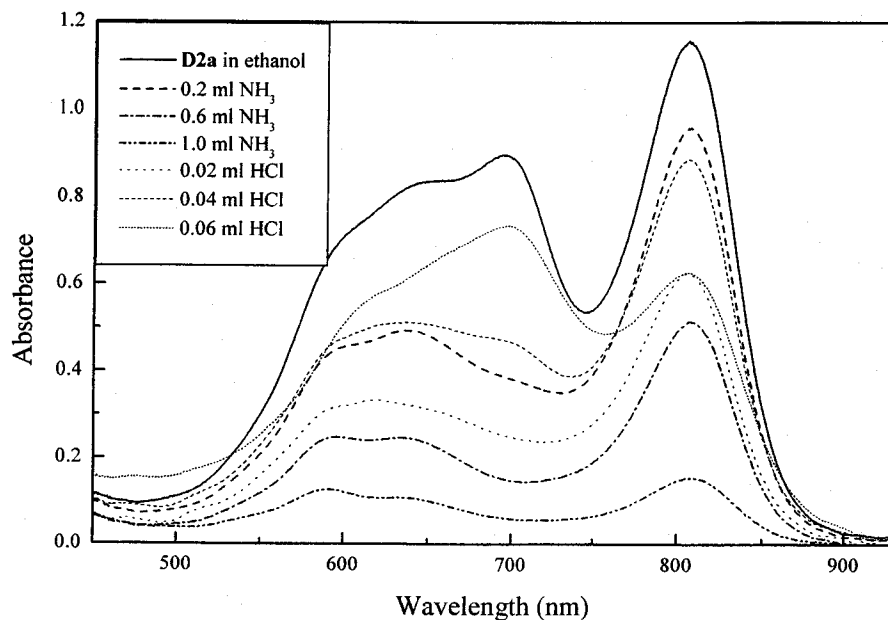

Fig. 4. Solution spectra of the dye D2a in the presence of ammonia and its reversibility by HCl.

[14]. 1,1-Bis(4-dimethylaminophenyl)ethylene was prepared from Michler's ketone [15].

2.2. Apparatus and procedures

Absorption spectra were recorded using an apparatus based on S1000 Ocean Optics CCD array spectrometer with spectral response from 450 to 930 nm.

Sensitivity to ammonia was tested by multiple addition of 0.2 ml of 2.5 wt.% aqueous solution of ammonia to 10 ml of ethanolic solution of the dye. The reversibility was tested by multiple addition of 0.02 ml of 35 wt.% HCl to the ammonia containing sample.

The pH was measured by pH-meter (OP-211/1, Radelkis) using the calomel and glass electrodes. An ethanol–water mixture 1:1 v/v was used as a solvent. The pH calibration has been carried out using the Radelkis and Merck pH standards. Due to dilution and the solvent change, the uncertainty of pH determination was approximately 0.5 pH unit. The values of pK_a were determined as inflex points of the curves depicting the dependence of absorbance at maximum wavelength on pH.

The structure of the dyes has been verified by nuclear magnetic resonance (NMR). NMR spectra were measured with a Varian VXR-300 spectrometer (300 MHz),
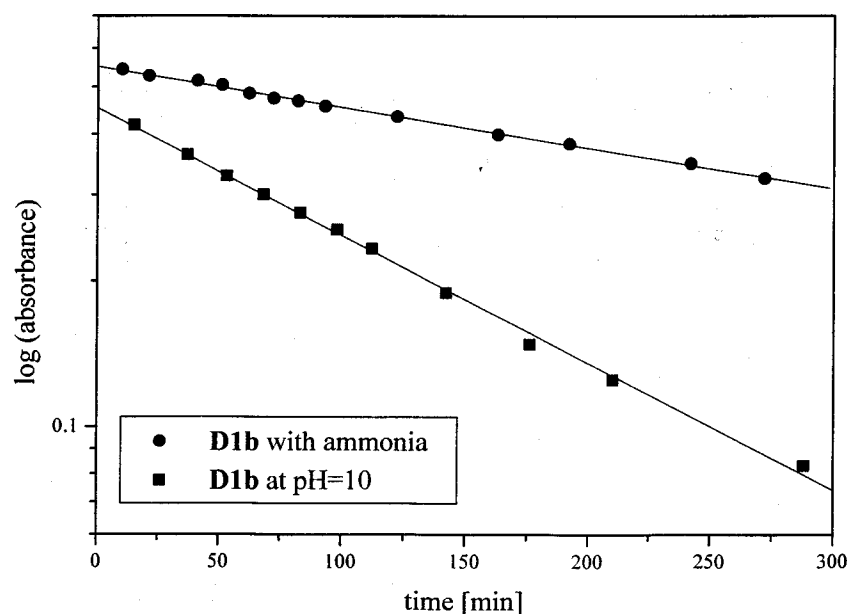
Fig. 5. Dependence of the peak absorbance at 714 nm on time for the dye D1b: (●)-addition of 1.3 ml of 2.5 wt.% ammonia water solution to 10 ml of the ethanolic dye solution; (■)-water–ethanol solution with pH 10.
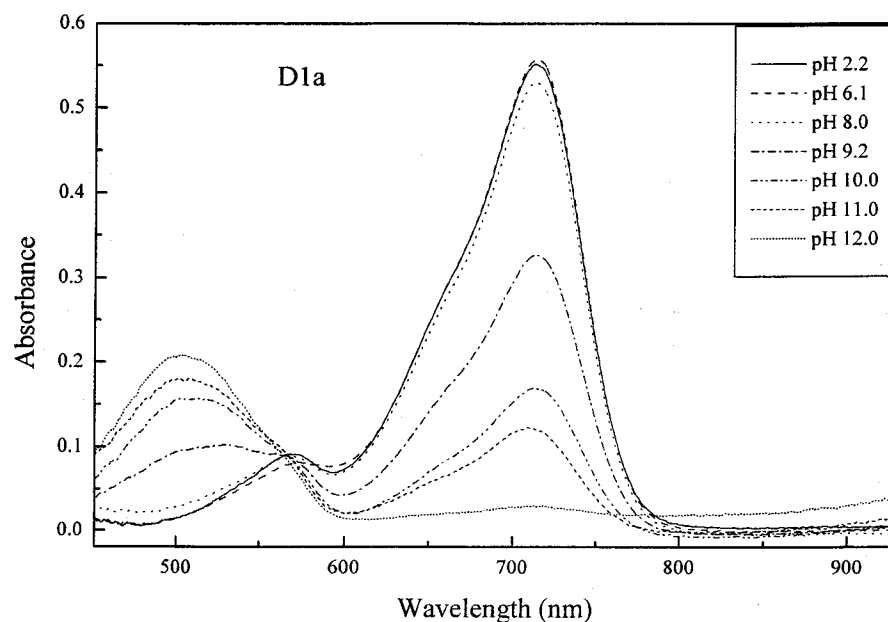

Fig. 6. pH dependence of spectra of the dye D1a in water–ethanol solution.

using TMS as internal standard and DMSO-d_6 as a solvent.

Differential scanning calorimeter DSC-7 (Perkin-Elmer) was used for the determination of thermal stabilities and melting points of the dyes.

3. Results and discussion

As stated above, our main effort is to develop NIR dyes that could be used as chemical transducers for distributed fibre optic ammonia sensors. The sensitivity of the selected members of both methine groups, D1a and D2a, is demonstrated in Figs. 3 and 4. It can be seen that both dyes are fully reversible to ammonia in the ethanol and ethanol–water solutions. The spectral response to ammonia of the other dyes reported in this paper is similar to those shown in Figs. 3 and 4. The response to ammonia is for all purposes immediate for all the dyes with the exception of the dye D1b. With this dye, the decrease of the absorbance depends on time and the interaction dye-ammonia obviously fol-
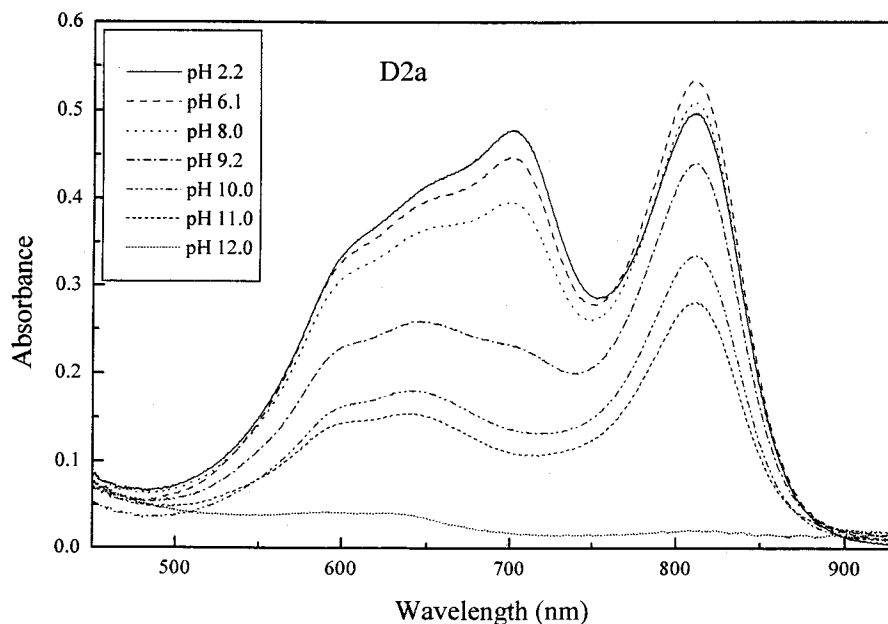
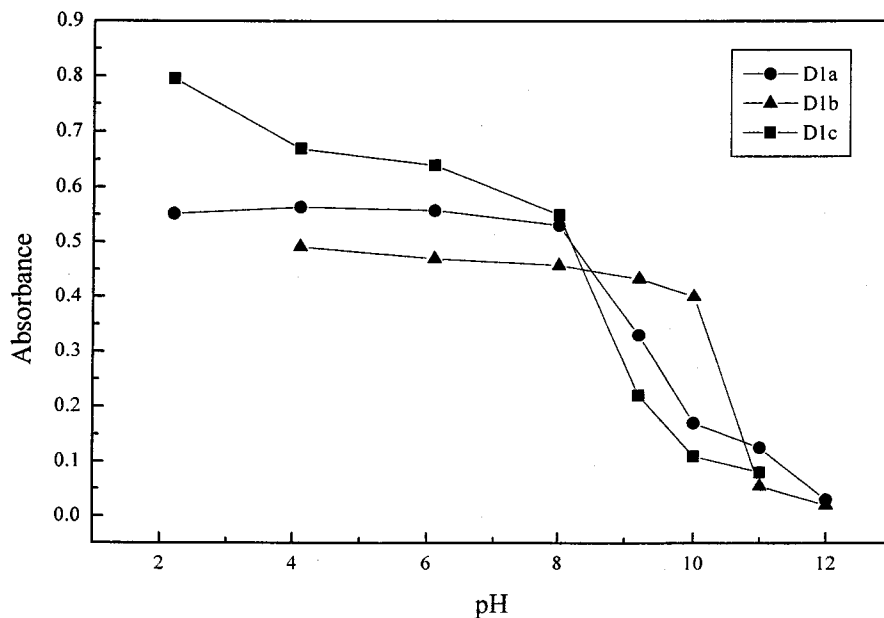Fig. 7. pH dependence of spectra of the dye D2a in water–ethanol solution.

Fig. 8. Absorbance at maximum wavelength as a function of pH for the dyes D1a-c in water–ethanol solution.

lows the first-order kinetics as shown in Fig. 5. Nevertheless, the original absorption spectrum of the dye can be recovered by adding HCl.

The dyes can be used also as pH indicators in the basic region. Figs. 6 and 7 show the dependence of the spectra of the dyes D1a and D2a on pH in water–ethanol solutions (1:1 v/v). Figs. 8 and 9 show that pK_a values are between 8.8–10.5 for the cyanine dyes and pK_a equals approximately 12 for the triphenylmethane dyes. The interaction with buffers suggests that ammonia is not the only agent capable of affecting the long

wavelength peak in the spectra. It can be seen in Fig. 5 that the response of the dye D1b is time dependent also in non-ammonia solutions. Some amines, such as triethylamine and dimethylcyclohexylamine, also interact with the dyes as it is demonstrated in Fig. 10 for the dye D1a.

Fig. 9 indicates that the absorbance of the peak at maximum wavelength for the dyes D2a-c decreases for pH < 3. This fact is more clearly demonstrated in Fig. 4 where it can be seen that addition of HCl to the ammonia-containing dye solution brings about an in-
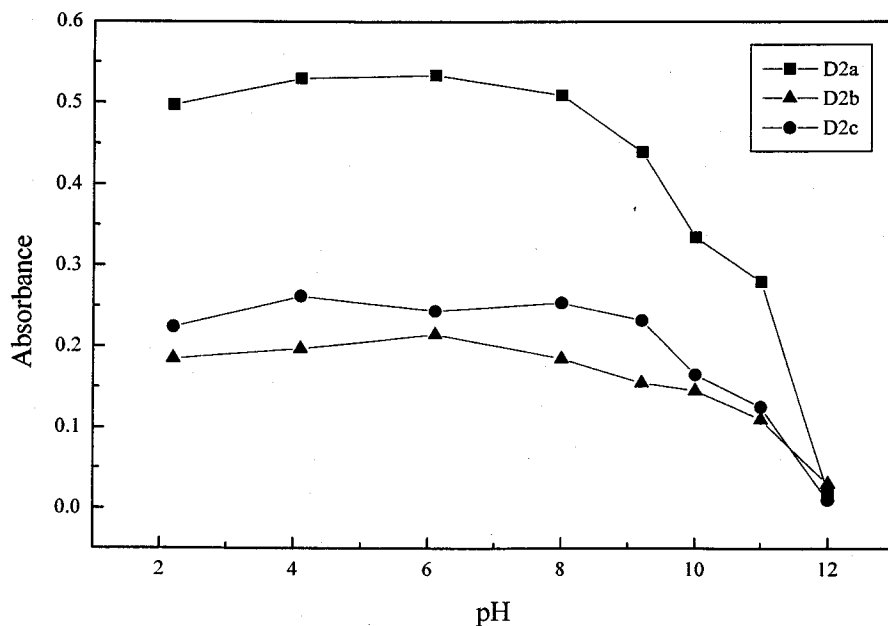
Fig. 9. Absorbance at maximum wavelength as a function of pH for the dyes D2a-c in water–ethanol solution.
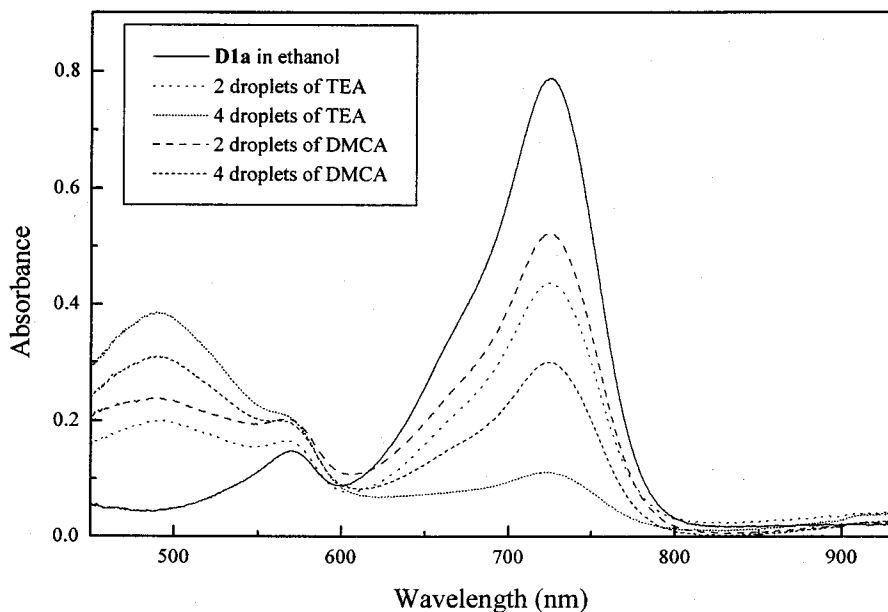

Fig. 10. Sensitivity of the dye D1a to triethylamine (TEA) and dimethyl-cyclohexylamine (DMCA). Volume of the dye solution was 3 ml.

crease of the peak. Further HCl addition led to the decrease of the absorbance.

The mechanism of the interaction of the dyes with ammonia is proposed in Fig. 11 for the dyes D1a-c. The lone electron pair of ammonia is probably attracted by the positive charge delocalised at the π-electron system of the dye. Formation of the bond between ammonia and the carbon skeleton breaks the conjugation which is manifested by the decrease of the peak at maximum wavelength. This mechanism

accounts for the fact that also other electron donors, such as OH^- ion or amines, interact with the dyes. The mechanism of interaction of ammonia with the dyes D2a-c is similar.

Figs. 3 and 4 show that the dyes are stable at the pH value close to 2. The DSC measurements have shown that the dyes are stable under air up to 150°C. These results indicate that the dyes can be incorporated in solid matrices via the sol-gel process or polymer thermo-curing.
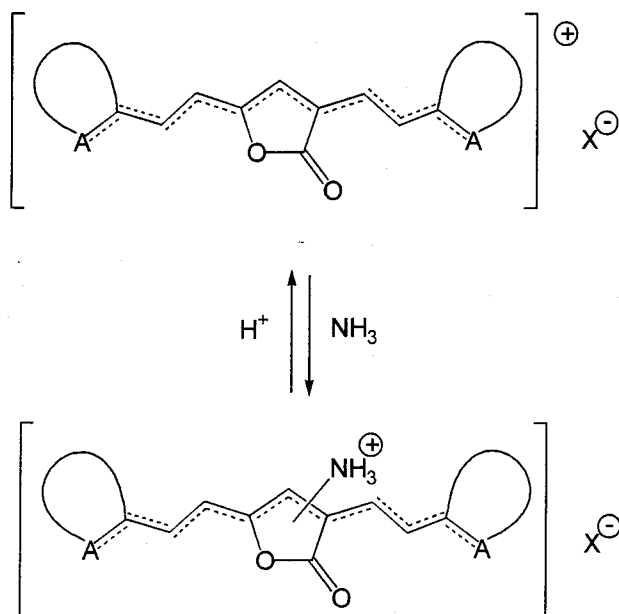
Fig. 11. Mechanism of interaction of the dyes D1a-c with ammonia.

4. Conclusion

The dyes D1a-c exhibit an absorption peak around 700 nm. The dyes D2a-c exhibit two peaks at approximately 700–810 nm. All the dyes presented are reversibly sensitive to ammonia and amines in ethanol and ethanol–water solutions. Further work is aimed at testing of these dyes incorporated in solid matrices.

Acknowledgements

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Biographies

Marian Landl is a research worker at the Faculty of Chemical Technology of Slovak Technical University in Bratislava. In 1992 he finished the study of organic chemistry. In 1992–95, during his Ph.D. study, he dealt with the synthesis of new types of oligothiophenes. At present, the main field of his scientific work is the synthesis of near infrared dyes used as chemical tranducers in fibreoptic sensors for various chemical agents.

Peter Šimon is a senior lecturer of thermodynamics at the Faculty of Chemical Technology of Slovak Technical University in Bratislava. In 1976 he finished the study of physical chemistry. In 1981 he defended his Ph.D. thesis concerning the degradation of polyvinyl chloride. The main fields of his scientific work are thermochemical properties of materials and study of reaction mechanisms.

Frank Kvasnik is a senior lecturer in optical sensing and imaging in the Department of Instrumentation and Analytical Science at UMIST. In 1976 he received the BSc degree in physics from the University of Manchester and in 1981 the Ph.D. in laser physics from the University of Manchester. His research interests include fibre optic sensors, laser spectroscopy, confocal microspectrometry and opto-electronic instrumentation.